

## TRANSMITTAL LETTER TO THE UNITED STATES

DESIGNATED/ELECTED OFFICE (DO/EO/US)

CONCERNING A FILING UNDER 35 U.S.C. 371

Muller-17

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/509400

INTERNATIONAL APPLICATION NO.

PCT/DE98/02860

INTERNATIONAL FILING DATE

25 September 1998

PRIORITY DATE CLAIMED

27 September 1997

## TITLE OF INVENTION

Aluminium Acetoacetate Compounds, the Production and Use Thereof as Printing Ink Additives

## APPLICANT(S) FOR DO/EO/US

Peter Finmans and Christina Diblitz

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☐ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☒ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

## Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☒ Certificate of Mailing by Express Mail
20. ☒ Other items or information:

Acknowledgment Postcard

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) <div style="font-size: 2em; font-weight: bold; margin-top: 5px;">09/509400</div>	INTERNATIONAL APPLICATION NO. <div style="font-weight: bold; margin-top: 5px;">PCT/DE98/02860</div>	ATTORNEY'S DOCKET NUMBER <div style="font-weight: bold; margin-top: 5px;">Muller-17</div>
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21. The following fees are submitted: <b>BASIC NATIONAL FEE ( 37 CFR 1.492 (a) (1) - (5) ) :</b>				CALCULATIONS    PTO USE ONLY	
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO .....				\$970.00	
<input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO .....				\$840.00	
<input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....				\$690.00	
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....				\$670.00	
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) .....				\$96.00	
<b>ENTER APPROPRIATE BASIC FEE AMOUNT =</b>				\$840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than _____ months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	30 - 20 =	10	x \$18.00	\$180.00	
Independent claims	2 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable). <input checked="" type="checkbox"/>				\$260.00	
<b>TOTAL OF ABOVE CALCULATIONS =</b>				\$1,280.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				\$0.00	
<b>SUBTOTAL =</b>				\$1,280.00	
Processing fee of \$130.00 for furnishing the English translation later than _____ months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
<b>TOTAL NATIONAL FEE =</b>				\$1,280.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				\$0.00	
<b>TOTAL FEES ENCLOSED =</b>				\$1,280.00	
				Amount to be: refunded	\$
				charged	\$

- ☒ A check in the amount of **\$1,280.00** to cover the above fees is enclosed.
- ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- ☒ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **02-4345** A duplicate copy of this sheet is enclosed.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO:

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\_\_\_\_\_  
 SIGNATURE  
**C. James Bushman**  
 \_\_\_\_\_  
 NAME  
**24,810**  
 \_\_\_\_\_  
 REGISTRATION NUMBER  
**March 27, 2000**  
 \_\_\_\_\_  
 DATE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
ACTING AS RECEIVING OFFICE FOR THE PCT

In re Application of § Attorney Docket No.: Muller-17  
Peter Finmans and Christina Diblitz §  
Int'l. Appln. No.: PCT/DE98/02860 §  
Int'l. Filing Date: 25 September 1998 §  
U.S. Serial No.: To Be Assigned §  
U.S. Filing Date: Herewith §  
For: *Aluminium Acetoacetate Compounds,* §  
*the Production and Use Thereof as* §  
*Printing Ink Additives* §

**PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Attn.: DO/EO/US

Sir:

Kindly amend the above-identified application as follows:

**In the Specification**

On page 1, below the title, insert the following subheadings:

--BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION--

On page 1, at line 6, insert the following subheading:

--DESCRIPTION OF THE PRIOR ART--

On page 1, in line 11, delete "Aluminium" and insert therefor "aluminium".

On page 1, in line 12, delete "acts" and insert therefor --act-- and delete "cross linking"

and insert therefor --a cross-linking--.

006490 00450550

On page 1, at line 21, insert the following paragraph:

--US 4,264,370 and GB-A-772 144 disclose mixtures containing glycol compounds, e.g., polyalkyl glycols, and aluminium compounds, with the aluminium compounds being manufactured by conversion of aluminium alcoholates with substoichiometric amounts of  $\beta$ -keto-carboxylates. The aluminium compounds according to US 4,264,370 and GB-A-771 144 always contain at least one alkoxylate group.--

On page 1, at line 26, insert the following subheading:

On page 2, in line 6, change “C1 to C12” to --C<sub>1</sub> to C<sub>12</sub>-- and change “C1 to C4” to --C<sub>1</sub> to C<sub>4</sub>--.

On page 2, in line 6, after “residue” and before the comma, insert --particularly a C<sub>1</sub> to C<sub>2</sub> alkyl residue--.

On page 2, in line 7, delete “comprises” and insert therefor --comprise--.

On page 2, in lines 7-8, delete the period after “group” and delete “R is particularly preferred for a C1 to C2 alkyl residue”.

On page 2, in line 9, change “C1 to C4” to  $--C_1$  to  $C_4--$ .

On page 2, in line 10, change “C1 to C2” to  $--C_1$  to  $C_2--$ .

On page 2 at line 12, insert the following subheading:

On page 3, in line 22, change “C1 to C6” to --C<sub>1</sub> to C<sub>6</sub>-- and change “C2 to C4” to --C<sub>2</sub> to C<sub>4</sub>--.

On page 3, in line 31, change “C1 to C18 or C1 to C6” to --C<sub>1</sub> to C<sub>18</sub> or C<sub>1</sub> to C<sub>6</sub>--.

On page 3, in line 32, change “C2 to C4” to  $-C_2$  to  $C_4$ --.

On page 6, in line 8, delete "crosslinked" and insert therefor --cross-linked--.

On page 6, in line 10, delete "As UV/EB curing of printing ink binders" and insert therefor --As printing ink binders cured by UV/EB--.

On page 7, in line 1, delete "crosslinking" and insert therefor --cross-linking--.

On page 7, in line 3, delete "crosslinking" and insert therefor --cross-linking--.

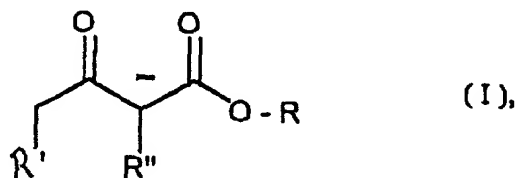
On page 7, in line 28, before "inoculation" delete "an".

### In the Claims

Please amend Claims 1-7 as follows:

1. (Amended) A Composition [containing] comprising:

(A) one or more aluminium compounds with [at least one] three ligands per aluminium atom of the following kind:



[whereby] wherein R [stands for] is a [C1] C<sub>1</sub>- to [C12] C<sub>12</sub>- hydrocarbon residue, which may comprise 1 to 4 ether linkages and/or one hydroxy group, [dd] and R' and R'', independent of one another, stand for H and/or one [C1] C<sub>1</sub>- to [C4] C<sub>4</sub>- hydrocarbon residue; and

(B) one or more glycol ether compounds.

2. **(Amended)** The [Compositions] composition according to [Claim] claim 1, wherein the aluminium compound (A) is contained in the composition [with] in at least 50% by weight, [preferably 75% by weight,] relative in each case to the sum of the components (A) and (B).

3. **(Amended)** The [Compositions] composition according to [one] any of [the above] claims 1 or 2, wherein the aluminium compound is aluminium tris(methyl-aceto acetate) and/or aluminium tris(ethyl-aceto acetate).

4. **(Amended)** The [Composition] composition according to [one] any of [the above] claims 1 or 2, wherein the glycol ether compound is a compound which comprises n  $-(X-O)-$  units, wherein X may be different for each n and stands for a substituted or unsubstituted saturated [C1] C<sub>1</sub>- to [C6, preferably C2 to C4,] C<sub>6</sub>- hydrocarbon, and n stands for an integer from 1 to 10[, preferably 2 to 4].

5. **(Amended)** The [Composition] composition according to [one of the above] claim[s] 4, wherein the glycol ether compound is dipropylene glycol-mono-n-butyl ether and/or diethylene glycol-mono-n-butyl ether.

6. **(Amended)** The [Composition] composition according to [one] any of [the above] claims 1 or 2, wherein the composition additionally contains polyester of poly-acrylic acid ester compounds.

7. (Amended) The [Composition] composition according to [one] any of [the above] claims 1 or 2, wherein the compound additionally contains colour-giving additives such as carbon black, inorganic pigments, organic pigments and/or soluble organic dyes.

Please cancel Claims 8-14.

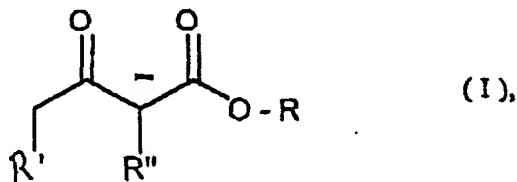
Please add the following new claims, 15-22:

- 15. A composition according to claim 4, wherein said substituted or unsubstituted saturated hydrocarbon contains 2 to 4 carbon atoms.

16. The composition of claim 4, wherein n is from 2 to 4.

17. The composition of any of claims 1 or 2 wherein aluminium compound (A) is contained in the composition in at least 75% by weight.

18. A method for the manufacture of an aluminium compound with at least one ligand per aluminium atom having the following structure:



wherein R is a C<sub>1</sub> to C<sub>12</sub> hydrocarbon residue, which may comprise 1 to 4 ether linkages and/or one hydroxy group, and R' and R'', independent of one another, stand for H and/or one C<sub>1</sub> to C<sub>4</sub>

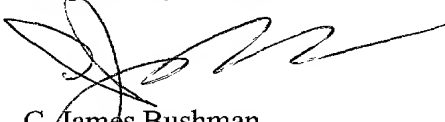
hydrocarbon residue comprising reacting a C<sub>1</sub> to C<sub>12</sub> aluminium alkylate with a 3-oxo-carbonic acid ester compound at a temperature of above 140°C in the presence of a glycol ether compound.

19. The method according to claim 18, wherein the temperature is above 160°C.
20. The method according to claim 18 wherein the temperature is above 140 °C for 1 to 10 hours during or after conversion.
21. The method according to claim 20 wherein the temperature is above 140°C for 4 to 8 hours.
22. A composition produced by any of claims 18-21.--

#### Remarks

In view of the foregoing amendments, it is respectfully submitted that all claims are in condition for allowance, which is hereby earnestly solicited and respectfully requested.

Respectfully submitted,

  
C. James Bushman  
Reg. No. 24,810

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#### CERTIFICATE OF EXPRESS MAILING

I, Jan C. Lipscomb, hereby certify that this correspondence and all referenced enclosures are being deposited by me with the United States Postal Service as Express Mail with Receipt No. EL010850996US in an envelope addressed to Box PCT, Assistant Commissioner for Patents, Washington, DC 20231, on March 27, 2000.

By: Jan C. Lipscomb



D-97012 PCT

WO 99/16739

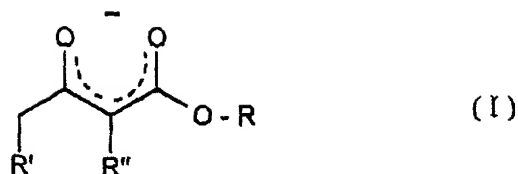
**Aluminium alkyl aceto acetate compounds, their manufacture and  
use as additives to printing inks**

The invention in question is concerned with compositions containing aluminium alkyl  
5 aceto acetate compounds, their manufacture and use as additives to printing inks.

The use of aluminium tris-acetyl acetate and aluminium tris-ethyl aceto acetate as a  
component in acrylate adhesives, silicone resins, intaglio inks and similar is known.  
For example, US 4,221,593 discloses the use of aluminium di-isopropoxide mono-  
10 ethyl aceto acetate and aluminium tris-ethyl aceto acetate as gelling agents for paint  
binders. Depending on the reaction conditions Aluminium tris-acetyl acetate and  
aluminium tris-ethyl aceto acetate acts as cross linking agent of the material in  
question. Systems treated in this way, have advantages in application. They have im-  
proved rheology, higher resistance against environmental and temperature influences  
15 or increased strength (hardness, adhesion properties). Aluminium tris-acetyl acetate  
has disadvantages with regard to the toxicity, high costs of raw materials, complicated  
synthesis, the solid aggregate state and the low solubility in all customary solvents.  
Aluminium tris-ethyl aceto acetate also has low solubility in all customary solvents  
and a high tendency to precipitation of solid matter as a result of crystallisation  
20 phenomena.

The task of the invention in question is to develop aluminium compounds which do  
not have any or at least most of the disadvantages described above. In particular, the  
compounds have to be suitable as additives for printing inks and correspondingly to  
25 have a high compatibility with printing ink binders, in particular for offset printing.

Surprisingly, it was found that aluminium compounds in certain solvents are suitable  
for this purpose. In the compositions according to the invention in question,  
aluminium compounds with at least one and at the most three, preferably three,  
30 ligands of the following kind are contained:



5 wherein

R stands for a C1 to C12, preferably a C1 to C4 hydrocarbon residue, which may comprises 1 to 4, preferably 1 to 2, ether linkages and/or one hydroxy group. R is particularly preferred for a C1 to C2 alkyl residue, and

10 R' and R'', independent of one another, stand for H and/or one C1 to C4 alkyl residue, preferably for H and/or one C1 to C2 alkyl residue.

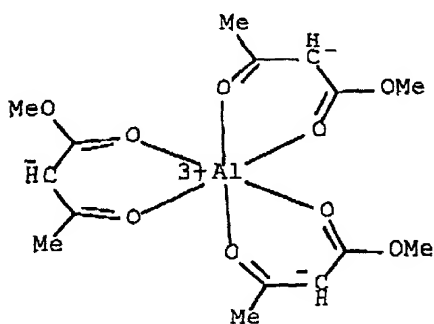
Glycol-ether compounds are used as further components in the composition.

15 Further, the aluminium compound can be a product of the above mentioned aluminium compounds (A) with compounds containing carboxyl (including acyl), ester, alcoholate or hydroxy groups, with the products being aluminium compounds which further have at least one of the above mentioned ligands (I).

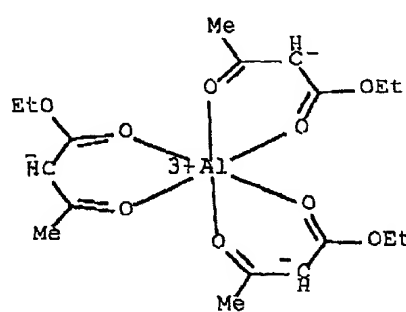
20 Aluminium tris(methyl-aceto acetate) II (= aluminium complex of 3-oxo-butane acid methyl ester [97494-08-1]), aluminium tris (ethyl aceto acetate) III [15306-17-9]

20

25



II



III

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aluminium tris (2-hydroxy ethoxy ethyl aceto acetate), aluminium tris(dodecyl aceto acetate) and aluminium tris(benzyl aceto acetate) are particularly suitable aluminium compounds.

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These aluminium compounds are accessible, for example, by means of derivatisation of aluminium alcoholates, preferably aluminium tri-isopropoxide by means of a ligand

exchange reaction. For this, aluminium tri-isopropoxide is converted, for example with an aceto-acetic acid ester compound.

One of the problems for the use of these aluminium compounds, in particular in the printing ink industry, is the selection of a suitable solvent. Mineral oils can be used here, although they have the disadvantage that the solubility of the aluminium compounds is limited and therefore only low contents of Al can be achieved. Suitable concentrations are under 4% by weight. The mineral oils frequently used in the printing ink industry with a boiling range from 240 to 310 °C do not lead to liquid products in many cases.

In addition, when selecting the solvent, attention must be paid to the fact that processing temperatures up to 200°C are achieved in some processes in the printing ink industry. The addition of low-boiling solvents such as low alcohols or an excess of aceto-acetic acid ethyl ester (ethyl aceto-acetate), which is contained as a further raw material component in the additive for this event, is thus ruled out.

It was surprisingly found that glycol-ether compounds are particularly suited as solvents for the above mentioned aluminium compounds. Glycol ether compounds within the meaning of the invention in question are oligomeric compounds which essentially have  $n(-X-O-)$  units, wherein X may be different for each n and stands for a saturated C1 to C6, preferably C2 to C4, substituted or unsubstituted hydrocarbon, which can be connected to (one or more) arbitrary carbon atom(s) and, optionally, can for example bear one or more further -O- connections (e.g. as =O, -OH or -OR''' group). n stands for an integer from 1 to 10, preferably from 2 to 8, particularly preferably 2 to 4. The glycol ether compounds preferably have exclusively carbon, hydrogen and oxygen atoms, but can, if need be, also have a further, different atom per molecule, for example.

The end groups of the glycol ether compounds (also the side chains) can be -H, -R''', -OH or -OR''' groups. R''' preferably stands for a C1 to C18 or C1 to C6, particularly preferably C2 to C4, hydrocarbon group, preferably an alkyl group, or for a glycol ether compound with 1 to 18 carbon atoms. Preferably, the endgroup are -OR''' and -H, relative to one molecule.

Further, the glycol ether compound can, if need be, also contain a C=O connection (per molecule), e.g. in the form of an ester connection (e.g. as -COOR''' or -OOCR''').



this, it is not so much the hydrolysis reaction with the air humidity (a reaction of the outer surfaces of the product with water only leads to a relatively slight acceleration of the crystallisation process) as the dust particles contained in the air which are considered to be the triggers for the crystallisation process.

5

The products obtained in this way have what is the unique and surprising property for Al-alcoholate derivatives of having a storage period in air of more than 6 months without opacity of the product being seen as a result of hydrolysis products or product crystals. The product is also flow-capable after this storage and has an Al content which has only inconsiderable deviations from the state at the beginning of the storage.

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To sum up, the product according to the invention has the following properties:

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- unique stability against hydrolysis
- fluid aggregate state despite unusually low concentration of solvents
- extraordinary properties both relative to usability for UV/EB curing of printing ink binders as well as for offset binders on the basis of alkyd resins, hydrocarbon resins and/or modified colophon resins.

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25

The rheology of printing ink binders is normally achieved by the composition according to the invention in question by an interaction, e.g. in the form of a connection/interlinking of COOH- or OH-functional groups with the aluminium compound. If the offer of such functional groups is large, a few AL centres (0.5 to 2, preferably about 1 Al atom per sum of COOH groups and -OH groups with acid numbers of up to about 10 mg KOH/g) are sufficient. If the acid number (and the OH number) of the resin to be thickened is lower than 10 mg MOH/g, a higher concentration of the derivative containing aluminium must be available in order to achieve the same effect (1 to 15 Al atoms per sum of -COOH- + -OH- groups) in order to increase the balance, i.e. the probability of an interaction between AL-O- and COOH- or OH- groups.

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Correspondingly, it is observed that the concentration of the aluminium compounds according to the invention in question used should, in printing ink binders low on COOH- and OH-, as frequently used in UV/EB curing systems on the basis of acrylic acid esters, beneficially be a factor of 5 to 15 higher than is customary in classical binders with involvement of alkyd and colophon-modified phenol resins.

In conventional binders such as alkyd resins, hydrocarbon resins and colophon-modified phenol resins, concentrations of preferably 0.3 to 2% by weight of the composition are used as an additive in the binder, particularly preferably 0.5% to 1.5% by weight (corresponding to roughly 0.03 to 0.1% by weight of aluminium in the binder). In UV/EB curing of printing ink binders, higher concentrations of additives of preferably 1 to 10% by weight of additive in the binder (corresponding to about an aluminium content of 0.06 to 0.6% by weight Al) are used, in order to build up crosslinked structures.

As UV/EB curing of printing ink binders only have a limited temperature resistance on the basis of their reactive double bonds (if the thermal limits are exceeded, there is a threat of premature hardening by polymerisation), the process of rheological modification at lower temperatures than in classical binders is to be carried out on the basis of alkyd resins and colophon-modified phenol resins. This results in low-reactive, relatively hydrolysis-stable Al-alcoholate derivatives not leading to a sufficient reaction speed.

In this context, it is surprising that the application of the aluminium alkyl acetoacetate compositions according to the invention in question in a polyester or acrylic acid ester based binder with acid and OH numbers  $< 2 \text{ mgKOH/g}$  leads to the most effective results with regard to the necessary Al concentration and the rheological properties of the binder.

Although the aluminium alkyl aceto-acetate compositions according to the invention in question possess a low reactivity, a much higher effectivity is achieved in relation to the Al content in this additive in the system examined than in all other state-of-the-art Al alcoholates or their derivatives.

The printing inks with additives according to the invention in question further contain colour-giving additives such as carbon black, inorganic pigments, organic pigments and/or soluble organic dyes. According to the invention, the printing inks with the additives are mainly used in offset printing. Such printing inks further contain polyester or poly-acrylic acid ester compounds as binders, preferably containing

suitable groups such as reactive double bonds for crosslinking by heat, electromagnetic radiation, in particular UV radiation, or electron rays. Alongside this, initiators for the corresponding crosslinking reaction must be contained in the printing inks. Printing inks equipped in this way guarantee drying in a matter of seconds.

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The compositions according to the invention in question are further suited for rheological modification of physically dry printing inks on the basis of alkyd resins, modified colophon resins or hydrocarbon resins.

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### Examples

#### Example 1

119.2 g of aluminium tri-isopropoxide (AIP) were mixed with 42.7 g of diethylene glycol-mono-n-butyl ether (DnB) and heated to 130 to 140°C. 227.8 ethyl acetoacetate (EAA) were added at sump temperatures up to 180°C in such a way that a distillative removal of 2-propanol (IPA) from the reaction mixture was achieved in parallel. The filtration resulted in a yellow-orange coloured clear product which formed crystals in storage in the air after about 4 days following addition of an inoculation crystal.

20

#### Example 2

419 g of AIP were presented at 100°C and mixed with dipropylene glycol-mono-n-butyl ether (DPnB). After heating to 130°C, EAA was added within 90 min. At the same time, IPA was removed distillatively. After the completion of the addition, distillation was carried out until the head temperature dropped. The sump temperature reached a maximum of 170°C. The subsequent filtration resulted in a clear, yellow product which formed crystals in the presence of an inoculation crystals in storage in the air within 4 weeks.

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### Example 3

1 mol aluminium-sec.butoxide (ASB) was heated to about 140°C and mixed with a mixture of 3 mol of methyl aceto acetate (MAA) and 80 g of DEnB. IPA was removed via the head. After this, the sump temperature was increased to 180°C with further  
5 distillation. After the target temperature had been reached, there was cooling and obtaining of a yellow-orange coloured product by filtration., In the presence of inoculation crystals and with storage in the air, the formation of a solid matter was observed after about 4 h.

### 10 Example 4

3 mol of AIP were mixed with 220 g of DPnB and heated to 190°C. 9 mol of EAA were added over a period of 5 h at this temperature and IPA simultaneously removed from the reaction mixture by distillation. After cooling and filtration, an orange-  
15 coloured, clear product with an Al concentration of 5.7% by weight was obtained, which could be stored in the air for 6 months in the presence of inoculation crystals without separation of solid matters being observed.

### Example 5

947 g of AIP were brought to a reaction with 1810 g of EAA within 1.5 h in such a  
20 way that distillate resulting was drawn off. After addition, the sump temperature was raised to 180°C, a vacuum applied to remove low-boilers and cooling to filtration temperature carried out. The filtration resulted in a product which can be dissolved in IPA. The Al concentration achievable in this in a storage-stable solution amounted to a maximum of 1% by weight.

25

### Example 6

Example 6 was carried out in the same way as Example 5, albeit with a final solution in a mineral oil section typical for printing inks in the boiling range of 260 to 290°C instead of IPA. Al concentrations about 3% by weight led to products which formed  
30 crystals within 24 h at room temperature.



#### Example 7

Example 7 was carried out in the same way as Example 1, albeit with the addition of DPnB after the reaction of AIP with EAA. The product obtained crystallised within a few hours after filtration and cooling.

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#### Example 8

A standard heat-set varnish on the basis of a phenol-modified colophon resin (3 parts) and an isophthalic acid based alkyd resin (2 parts) and a mineral oil with a boiling range of 260 to 290°C (3 parts) were mixed with 0.6 to 2.5% by weight of the product from Example 4 at a temperature of 180°C in intensive agitation, left at this temperature for 15 - 60 minutes and then cooled. The resin mixture had an acid figure of about 10 and an OH figure of about 30. The additive turned the varnish with a Newton's flow property into a homogeneous and viscous-structured binder with flow limit. The exact rheological properties were achieved by slight variation of the concentration of additive in the required way.

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#### Example 9

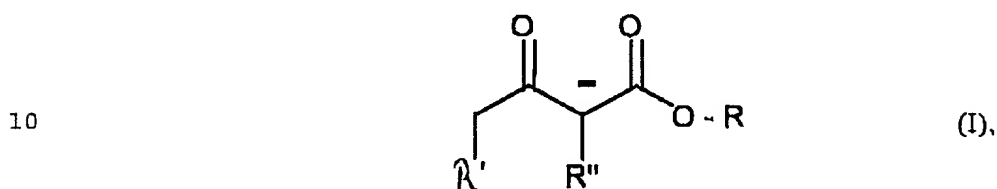
A UV/EB hardenable acrylate resin (acid figure < 2 mgKOH/g, OH figure < 2 mgKOH/g, Newton's rheology) was heated to a temperature of 100°C in the presence of 1 - 5% by weight of the product obtained in Example 4. The result was a binder for printing ink marked by a strong viscosity of structure, the rheology of which could be adapted to the requirements by corresponding adjustment of the Al content.

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# Patent claims

## 1. Composition containing

- 5 (A) one or more aluminium compounds with at least one ligand per aluminium atom of the following kind



whereby

15 R stands for a C1 to C12 hydrocarbon residue, which may comprise 1 to 4 ether linkages and/or one hydroxy group, and

and

R' and R'', independent of one another, stand for H and/or one C1 to C4 hydrocarbon residue and

- 20 (B) one or more glycol ether compounds.

2. Compositions according to Claim 1, wherein the aluminium compound (A) is contained in the composition with at least 50% by weight, preferably 75% by weight, relative in each case to the sum of the components (A) and (B).

- 25 3. Compositions according to one of the above claims, wherein the aluminium compound is aluminium tris(methyl-aceto acetate) and/or aluminium tris(ethyl-aceto acetate).

- 30 4. Composition according to one of the above claims, wherein the glycol ether compound is a compound which comprises n  $-(\text{X}-\text{O})-$  units, wherein X may be different for each n and stands for a substituted or unsubstituted saturated C1 to C6, preferably C2 to C4, hydrocarbon, and n stands for an integer from 1 to 10, preferably 2 to 4.

- 35 5. Composition according to one of the above claims, wherein the glycol ether compound is dipropylene glycol-mono-n-butyl ether and/or diethylene glycol-mono-n-butyl ether.

6. Composition according to one of the above claims, wherein the composition additionally contains polyester or poly-acrylic acid ester compounds.
- 5 7. Composition according to one of the above claims, wherein the compound additionally contains colour-giving additives such as carbon black, inorganic pigments, organic pigments and/or soluble organic dyes.
- 10 8. Method for the manufacture of the composition according to one of the above claims, wherein the composition is manufactured by conversion of a C1 to C12 aluminium alcoholate with a 3-oxo-carbonic acid ester compound at temperatures of above 140°C, preferably above 160°C in the presence of a glycol ether compound.
- 15 9. Method according to claim 8, wherein the product / the composition is kept at above 140°C for 1 to 10 h, preferably for 4 to 8 h, during or after the conversion.
- 10 10. Composition, manufacturable according to one of the procedures according to claims 8 to 9.
- 20 11. Use of the composition according to the claims 1 to 7 and 10 as an additive for colour-giving compositions.
12. Use according to claim 11 as an additive for printing inks.
- 25 13. Use according to claim 11 as an additive for radiation-curing or electron-beam-curing of printing inks.
- 30 14. Use according to one of the claims 11 to 13, wherein the composition is used in a concentration of 0.2 to 10% by weight relative to the binder in the colour-giving composition.

**COMBINED DECLARATION AND POWER OF ATTORNEY**

(ORIGINAL, DESIGN, NATIONAL STAGE OF PCT, SUPPLEMENTAL, DIVISIONAL,  
CONTINUATION OR CIP)

As a below named inventor, I hereby declare that:

**TYPE OF DECLARATION**

This declaration is of the following type: (check one applicable item below)

- ☐ original  
☐ design  
☐ supplemental

*NOTE: If the declaration is for an International Application being filed as a divisional, continuation or continuation-in-part application do not check next item, check appropriate one of last three items*

- ☒ national stage of PCT

*NOTE: If one of the following 3 items apply then complete and also attach ADDED PAGES FOR DIVISIONAL, CONTINUATION OR CIP*

- ☐ divisional  
☐ continuation  
☐ continuation-in-part (CIP)

**INVENTORSHIP IDENTIFICATION**

**WARNING:** *If the inventors are each not the inventors of all the claims an explanation of the facts, including the ownership of all the claims at the time the last claimed invention was made, should be submitted.*

My residence, post office address and citizenship are as stated below next to my name, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

**TITLE OF INVENTION**

**ALUMINIUM ACETOACETATE COMPOUNDS,  
THE PRODUCTION AND USE THEREOF  
AS PRINTING INK ADDITIVES**

**SPECIFICATION IDENTIFICATION**

the specification of which (complete (a), (b) or (c))

- (a) ☐ is attached hereto  
(b) ☒ was filed on March 27, 2000, as (x) Serial No. 09/509,400  
or ☐ Express Mail No., as Serial No. not yet known \_\_\_\_\_  
and was amended on \_\_\_\_\_ (if applicable)

*NOTE: Amendments filed after the original papers are deposited with the PTO which contain new matter are not accorded a filing date by being referred to in the declaration. Accordingly, the amendments involved are those filed with the application papers or, in the case of a supplemental declaration, are those amendments claiming matter not encompassed in the original statement of invention or claims. See 37 C.F.R. §1.67*

(c) (x) was described and claimed in PCT International Application No. PCT/DE98/02860, filed on 25 September 1998, and as amended under PCT Article 19 on

### ACKNOWLEDGMENT OF REVIEW OF PAPERS AND DUTY OF CANDOR

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a)

( ) In compliance with this duty there is attached an information disclosure statement. 37 CFR §1.97.

PRIORITY CLAIM

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed.

(complete (d) or (c))

(d) ☐ no such applications have been filed.

(e) (x) such applications have been filed as follows.

**NOTE** Where item (c) is entered above and the International Application which designated the U.S. claimed priority check item (e), enter the details below and make the priority claim

EARLIEST FOREIGN APPLICATION(S), IF ANY FILED WITHIN 12 MONTHS  
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

COUNTRY	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
Federal Republic of Germany	19742828 2	27 September 1997	Yes

ALL FOREIGN APPLICATION(S), IF ANY FILED MORE THAN 12 MONTHS  
(6 MONTHS FOR DESIGN) PRIOR TO THIS U.S. APPLICATION

# POWER OF ATTORNEY

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith. (List name and registration number.)

C. James Bushman, Reg. No. 24,810, Loren G. Helmreich, Reg. No. 29,389;  
Carlos A. Torres, Reg. No. 24,264; Marvin B. Eickenrodt, Reg. No. 18,541;  
and Eugene N. Riddle, Reg. No. 18,541

- ( ) Attached as part of this declaration and power of attorney is the authorization of the above-named attorney(s) to accept and follow instructions from my representative(s).

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DIRECT TELEPHONE CALLS TO  
(Name and telephone number)

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(713) 266-5593

## DECLARATION

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon

### SIGNATURE(S)

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CHECK PROPER BOX(ES) FOR ANY OF THE FOLLOWING ADDED PAGE(S) WHICH  
FORM A PART OF THIS DECLARATION

- ☐ Signature for third and subsequent joint inventors. Number of pages added \_\_\_\_.
- ☐ Signature by administrator(trix), executor(trix) or legal representative for deceased or incapacitated inventor. Number of pages added \_\_\_\_.
- ☐ Signature for inventor who refuses to sign or cannot be reached by person authorized under 37 CFR §1.47. Number of pages added \_\_\_\_.

\* \* \*

- ☐ Added pages to combined declaration and power of attorney for divisional, continuation, or continuation-in-part (CIP) application.
- ☐ Number of pages added \_\_\_\_.

\* \* \*

- ☐ Authorization of attorney(s) to accept and follow instructions from representative.

\* \* \*

If no further pages form a part of this Declaration then end this Declaration with this page and check the following item:

- ☒ This declaration ends with this page.